



Short communication

A novel nano structured LiFePO_4/C composite as cathode for Li-ion batteriesHuang Zhang^a, Dong Liu^b, Xiuzhen Qian^a, Chongjun Zhao^a, Yunlong Xu^{a,*}^a Key Laboratory for Ultrafine Materials of Ministry of Education, Shanghai Key Laboratory of Advanced Polymeric Materials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, PR China^b Department of Materials Science and Engineering, University of Texas at Arlington, Arlington, TX 76019, USA

H I G H L I G H T S

- LiFePO_4 nanowire was grown on the skeleton of carbon aerogel.
- The composite has a 3D network structure.
- The composite materials were tested as Li^+ -battery cathodes.
- The material has a capacity of 139.3 mAh g^{-1} at 10°C rate.
- The capacity retention is near 100% after 50 cycles.

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A novel network LiFePO_4/C composite was prepared by mixing precursor solution with carbon aerogel (CA) via a simple solution impregnation method, characterized by XRD, SEM, EDS and electrochemical analysis. The results revealed that the LiFePO_4 nanowire forming on the skeleton of CA intertwined with $\text{LiFePO}_4/\text{CA}$ particles and formed a special web structure. The initial discharge capacity was improved to be 139.3 mAh g^{-1} at 10°C and the capacity retention is near 100% after 50 cycles. The web structure could improve electron transport and electrochemical activity effectively.

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1. Introduction

In recent years, lithium-ion battery has quickly occupied the portable electronics market, and is under development for electric vehicles (EVs), hybrid electric vehicles (HEVs) and plug-in hybrid electric vehicles (PHEVs) [1]. Lithium iron phosphate with an ordered olivine-type structure, LiFePO_4 , has attracted extensive attention due to low cost, safety and high compatibility with environment [2]. However, the low electronic conductivity ($\sim 10^{-9} \text{ S cm}^{-1}$) [3] and lithium-ion diffusivity ($\sim 10^{-18} \text{ cm}^2 \text{ s}^{-1}$) [4] limit its commercial applications. Many researchers have suggested solutions to this problem as follows: (a) coating with a conductive

additives [5,6]; (b) ionic substitution to enhance the electrochemical properties [7,8]; and (c) synthesis of particles with well-defined morphology [9].

Mesoporous carbon with 3D and continuous conductive network structure may be a good candidate for the conductive additives. Li [10] prepared $\text{LiFePO}_4/\text{multi-walled carbon nanotubes}$ with a 3D network structure and such structure renders better electronic conductivity and discharge capacity. Sinha [11] utilized the polymer as template to prepare porous LiFePO_4/C with the pore size of 4–50 nm, revealing high discharge-rate capacity and excellent cycle stability. Whittingham [12] indicated that the added MWCNTs in pure LiFePO_4 enhanced the electronic conductivity of the final product. Likewise, Yang [13,14] used the unfolded graphene as a 3D conducting network for LiFePO_4 nanoparticles growth and synthesizes the porous $\text{LiFePO}_4/\text{graphene}$ composite materials. These LiFePO_4/C materials with a three dimensional

* Corresponding author. Tel./fax: +86 21 64252019.

E-mail address: xuyunlong@ecust.edu.cn (Y. Xu).

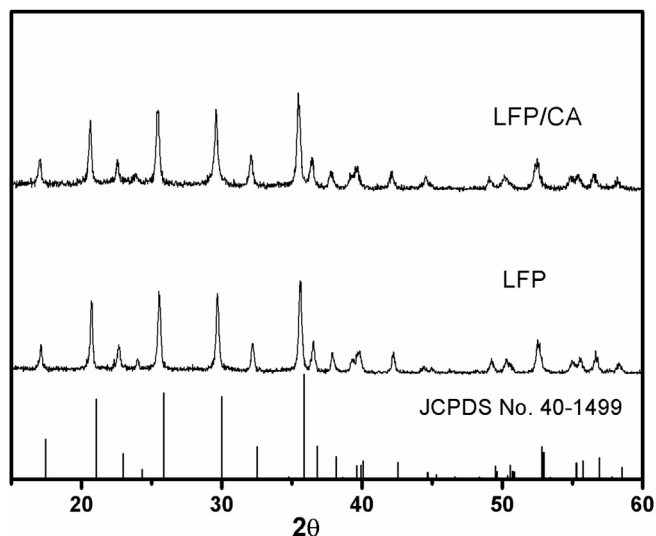


Fig. 1. XRD pattern of LFP and LFP/CA.

structure formed by LFP nanoparticles and graphene exhibit higher discharge capacities and more outstanding cycle stability. Also, a nanowire structured $\text{LiFePO}_4/\text{CNTs}$ composite was developed by Yang [15] and exhibited a promising application for high rate performance lithium ion batteries. What's more, engineering nano structured porous electrode material has become a key to high performance rechargeable lithium battery owing to its sustainable advantages in fast mass and charge transport [16–18].

Our previous work disclosed that carbon aerogel makes remarkable electronic conduction contribution to the performance of LiFePO_4 under high charge/discharge rate [19,20]. In this study, CA was added to tune the structure of LiFePO_4 and the electrochemical behaviors of as-prepared material at high rate were investigated.

2. Experimental

The carbon aerogel (CA) was prepared through a sol–gel method according to Ref. [21]. After grinding and sifting process, CA

was chemically oxidized by nitric acid to enhance its hydrophility. Stoichiometric amounts of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Sinopharm Chemical Reagent Co. Ltd, AR) and LiH_2PO_4 (Shanghai China Lithium Industrial Co. Ltd, GR) were dissolved in de-ionized water to form a saturated solution at room temperature. Then the carbon aerogel was immersed with above solution and ultrasonicated for 5 min. The solid–liquid mixtures were first dried under the irradiation of an infrared light for 12 h and then calcined at 600°C for 3 h (2°C min^{-1}) under a reductive atmosphere (90% Ar and 10% H_2). The LFP/CA was obtained and LiFePO_4 (LFP) was prepared under the same conditions.

The phase identification of powders was conducted with X-ray diffraction measurement (XRD, D/MAX 2550V, Japan) using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15423 \text{ nm}$). The sample was also evaluated by field emission transmission electron microscopy (FETEM, JEM-2010F, Japan), field emission scanning electron microscopy (FESEM, Hitachi S-4800, Japan) and energy dispersive spectroscopy (EDS), dispersed on a silicon substrate. Study of the electrochemical properties of samples was performed by assembling 2032 coin cells. The composite electrodes were prepared by mixing LFP or LFP/CA composite with carbon black and polyvinylidene fluoride (PVDF) in a weight ratio of 80:10:10 in NMP. The cells were assembled in an Argon-filled glove box (Super1220/750, Mikrouna) using lithium metal as anode electrode, a polypropylene microporous film (Cellgard2400) as the separator, 1 M LiPF_6 in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1, v/v) (Guangzhou Tinci) as the electrolyte. The LAND battery program control cell tester (LAND CT2001A, Wuhan, China) was used to perform the galvanostatic charge/discharge tests. Electrochemical impedance spectroscopy measurements were performed on an Electrochemical Workstation (CHI660D, Shanghai, China). The spectrum was potentiostatically measured by applying an ac voltage of 5 mV over the frequency range from 10^5 Hz to 10^{-2} Hz . The collected EISs were fitted using ZSimpWin software.

3. Results and discussion

Fig. 1 shows the XRD patterns for pure LiFePO_4 and $\text{LiFePO}_4/\text{CA}$ composite. All the patterns can be indexed to a single phase material having an orthorhombic olivine-type structure with a space group of

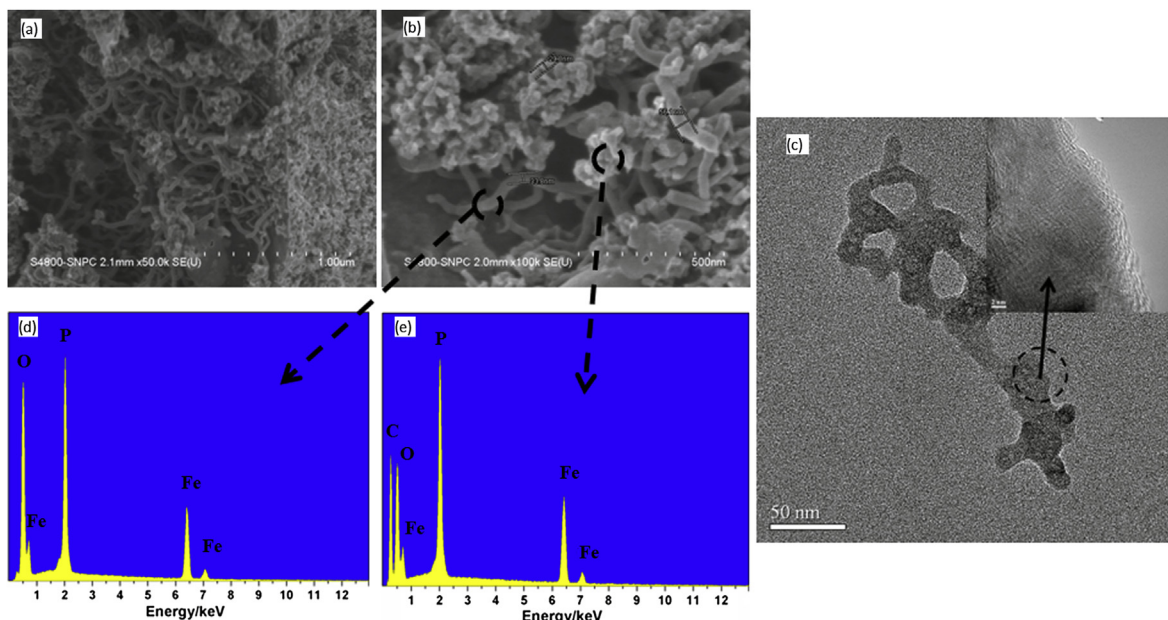


Fig. 2. SEM (a, b), HR-TEM (c) and EDS (d, e) images of LFP/CA.

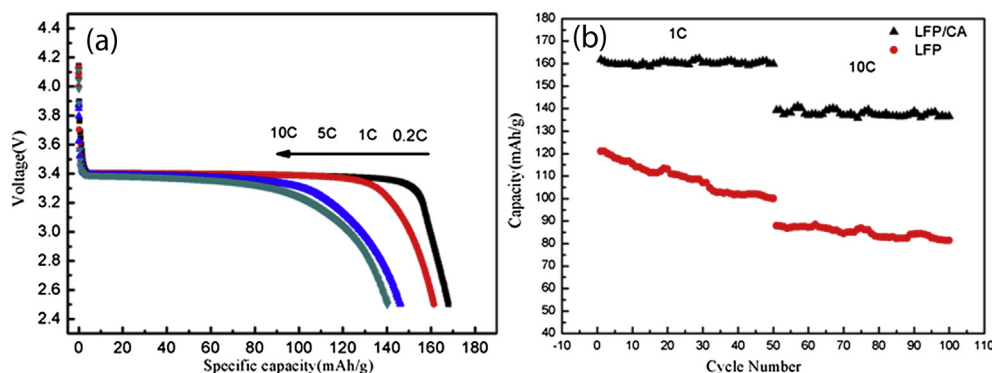


Fig. 3. Discharge curves (a) and cycle stability (b) of LFP at various rates.

Pnma, which is the same as the standard one (JCPDS card No. 40–1499). No impurity diffraction peak was detected, suggesting that the CA is believed to be present as amorphous carbon or low degree of crystallinity.

Fig. 2 shows the SEM, TEM and EDS images of LFP/CA. It can be observed from the SEM images that the LiFePO_4 nanowire and CA particles are coexisted in the composites. The nanowire growth on surface of mesoporous CA as substrate may be attributed to the packing of atoms and molecules along energetically preferential directions during the sintering process and stress-induced recrystallization which is sensitive to the high surface energy and strong adsorbability of nano/mesoporous CA [22–25]. LiFePO_4 nanowire can increase the effective contact area between active materials and electrolyte which is more conducive to the high rate performance of LiFePO_4 cathode. The TEM images show that LiFePO_4 particles are partially embedded into the pores of CA and that exhibits a carbon nano-network structure which leads to electronic continuity between particles. The LFP NWs intertwine with $\text{LiFePO}_4/\text{CA}$ particles together to form a three-dimensional network. EDS spectra in Fig. 2(d) and (e) indicate that Fe, P, O elements are existed in the nanowire and the CA particles contain Fe, P, O and C elements. The additive amount of CA is about 30 wt.%, which is proved by the EDS data.

Fig. 3(a) shows the initial discharge curves of LFP/CA at various rates. It can be seen that, in the potential range of 2.5–4.2 V, the discharge capacity of 0.2 C, 1 C, 5 C and 10 C are 168.3 mAh g^{-1} , 161.1 mAh g^{-1} , 146.5 mAh g^{-1} and 139.3 mAh g^{-1} , respectively. The LFP/CA material remains a high capacity when the discharge rate increases to 10 C. The comparison of cycle stability between LFP and LFP/CA is presented in Fig. 3(b). LFP/CA composite displays more

stable discharge capacity retention than LFP until 50 cycles at both at 1 C and 10 C and the high rate cycle stability is prominent without significant decay. The remarkably improved electrochemical performances can be attributed to the extraordinary 3D network structures [19,20,26,27].

To provide more information for the improved electrochemical property, AC impedance measurements are performed on all the samples at the charged state after cycling. In Fig. 4, the impedance spectra were combinations of a depressed semicircle in high frequencies and a straight line in low frequencies. The symbols R_e , R_f , R_{ct} and W are denoted the bulk resistance, contact resistance, charge–transfer resistance and Warburg impedance, respectively. The high frequency intercepting at the real axis corresponds to the bulk resistance (R_e) of the cell, which reflects the electronic conductivity of the electrolyte, separator and electrode. The high frequency semicircle may be caused by the contact resistance (R_f) including current collector-to-particles and the particle-to-particle contact resistance of the LiFePO_4/C cathode. The second medium-frequency semicircle is attributed to the charge–transfer reaction resistance (R_{ct}) in the LiFePO_4/C cathode–electrolyte interface. The straight line in the low frequency region is related to Warburg impedance (W) that is associated with Li^+ diffusion through the LiFePO_4/C cathode. [28] Comparing the semicircles of the pure and CA coated samples in the moderate frequency region, it is evident that the total electric resistance was decreased by CA coating. Specifically, the Nyquist plots are fitted using the equivalent circuit as shown in Fig. 4. It can be seen from Table 1 that all the R_e , R_f and R_{ct} of NWs LFP/CA composite are smaller than those of pure LFP. The R_e values of LFP/CA and LFP are 9.4Ω and 11.2Ω , respectively. Nevertheless, the R_f and R_{ct} values decrease from 38.8Ω to 14.3Ω and 456.1Ω to 108.7Ω after coating with CA, which shows the special 3D conducting network structure has more pronounced effect on the contact resistance and the charge–transfer reaction resistance in the electrode–electrolyte interface. The reason is probably due to the high electronic conductivity of the CA additive and efficient contact between electrochemical active particles. These results are in good agreement with our previous report [19].

4. Conclusions

The nanowire $\text{LiFePO}_4/\text{CA}$ composites have been synthesized successfully via a solution impregnation method followed by heat

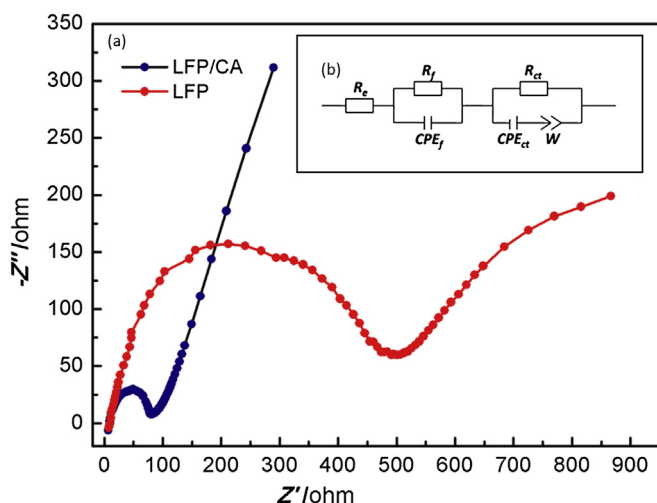


Fig. 4. Nyquist plots of LFP and LFP/CA materials (a), the equivalent circuit (b).

Table 1

Impedance parameters derived using equivalent circuit model for the LFP and LFP/CA.

Temperature	Sample	$R_e(\text{ohm})$	$R_f(\text{ohm})$	$R_{ct}(\text{ohm})$
20 °C(RT)	LFP	11.2	38.8	456.1
	NWs LFP/CA	9.4	14.3	108.7

treating. The $\text{LiFePO}_4/\text{CA}$ composite has the phospho-olivine structure as the bare one. By this method, the added CA causes the growth LiFePO_4 nanowire and increases the electronic conductivity. The formation of 3D nano-network due to the nanowire and CA increases the contact area between active materials and electrolyte. Thus both the specific capacity and the cycle stability of LiFePO_4 at high discharge rate can be significantly improved. The research is of potential interest to application of mesoporous carbon as a new conducting additive in cathode preparation and to development of high-power lithium ion batteries for hybrid electric vehicles.

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